

CONTAMINATION OF SEDIMENTS IN CENTRAL PART OF SETO INLAND SEA, JAPAN

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ABSTRACT

To investigate the contamination degree of sediments, core and surface sediment samples were obtained from 44 site locations in Seto Inland Sea, a typical closed sea of Japan. The physical properties, such as water content, grain size, specific gravity of particles, ignition loss and content of carbonate of the samples were measured. At the same time, the concentrations of heavy metals, PCB, pesticide and organotin compounds of the sediment samples were measured. The results showed that the concentrations of copper, zinc and lead were relatively high near coast and river mouth, in comparison to other sediments obtained from the middle parts of Seto Inland Sea. The concentration of organotin compounds was relatively high in a small narrow bay. However, PCB and pesticide were not detected.

RÉSUMÉ

Dans le but d'établir le niveau de contamination des sédiments, des échantillons ont été prélevés à la surface et au centre des sédiments dans 44 sites de Seto Inland, une mer intérieure typique du Japon. Les propriétés physiques, telles que l'humidité, la granulométrie, la gravité spécifique des particules, la perte causée par l'ignition, ainsi que le contenu carbonique des échantillons ont été déterminées. Par la même occasion, les concentrations de métaux lourds, de BPC, de pesticides et de composés d'organotin ont été analysés à partir d'échantillons prélevés. Les résultats ont démontré des concentrations relativement élevées de cuivre, de zinc et de plomb près de la côte et à l'embouchure de la rivière, comparativement aux sédiments obtenus au milieu de la mer Seto Inland. La concentration des composés d'organotin est relativement élevée dans la petite baie. Cependant, les PBC et les pesticides n'y ont pas été détectés.

1. INTRODUCTION

After the industrial revolution, the substances discharged into the environment have been accumulated into marine sediments (Matsumoto, 1983, Matsumoto et al, 1983, Fukue, et al, 1995, 1996, 1999, Yamagata, 1978, Iwata et al, 1994). Some of pollutants discharged into sea are taken by phytoplankton, which is taken by zooplankton. The dead bodies of phytoplankton and zooplankton deposit on seafloor. On the other hand, some pollutants are adsorbed on suspended particles, because of high adsorption of the particles. It is well known that clay minerals and organic matter have high adsorption capacity (Yong et al, 1992).

The plankton becomes the bait of benthos and fishes. Some benthos and fishes eat organic and inorganic fine particles. The inorganic particles adhered organic matter on their surfaces. Although inorganic particles will be excreted from their body, the adhered organic materials and adsorbed hazardous substances will possibly be taken in their bodies.

The desorption of substances from the particles is strongly influenced by pH value of the surrounding liquids. In general, soil particles will tend to release the adsorbed substances at the decreased pH value (Yong et al, 1992). Therefore, it is considered that a low pH value of the gastric juice of living things plays an important role on the bio-concentration.

Thus, marine sediments become the starting point of a food chain for marine living things. As far as the bio-concentration is concerned, sediment quality will be one of the serious problems not only for sea animals, but also for human beings. With a food chain, the biological concentration in sea is complicated in comparison to that occurred in land. Oceanographical studies show that hazardous substances, such as heavy metals and PCB, are accumulated in most sea animals (Tanabe et al, 1998).

The excess daily intake of the hazardous substances for seafood results from the contamination of seawater and marine sediments. As far as sediment quality is concerned, the following information is needed;

- 1) kind and concentration of substances,
- 2) background values of the substances required for evaluation and safety criterion and
- 3) the contaminated thickness required for treatment or dredging.

These will also be required to develop techniques for cleanup of sea bottom. In this study, the contamination of sediments in Kasaoka bay and the surrounding sea area is discussed as a case study of the site investigation.

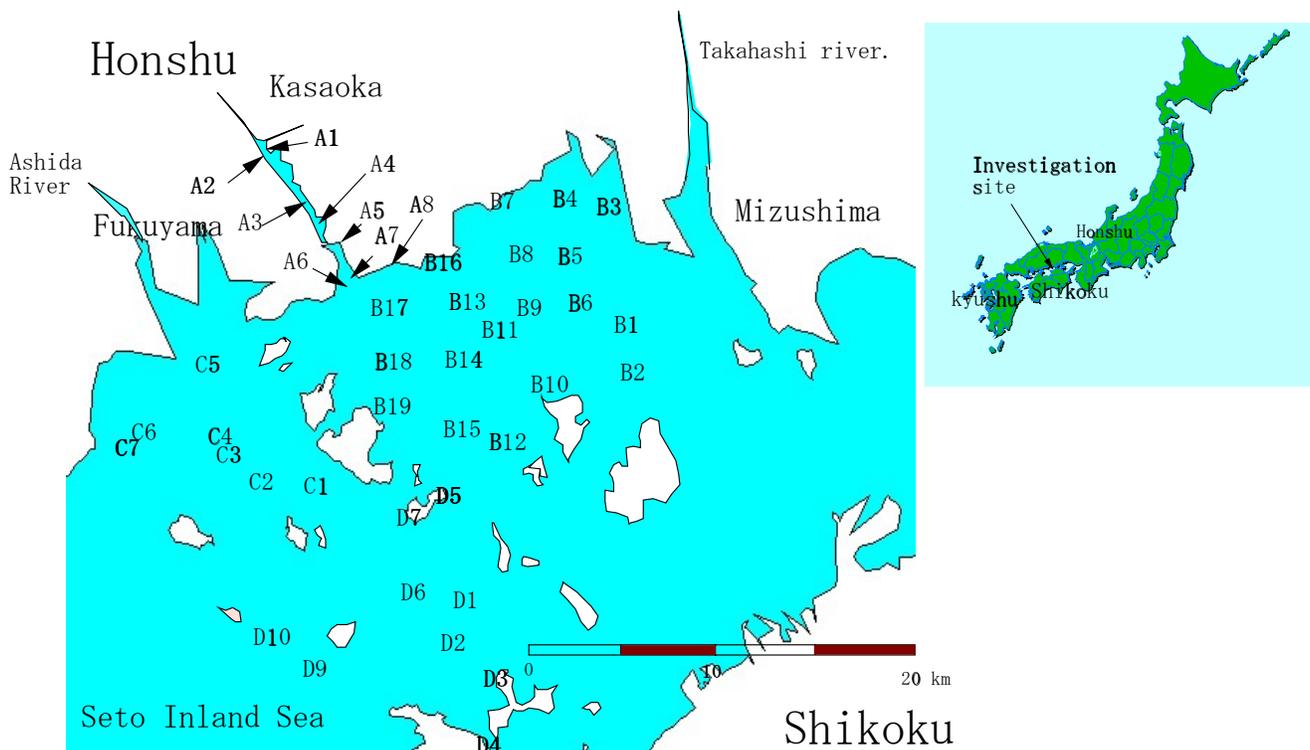


Figure 1. Sampling site locations of sediments in Seto Inland Sea.

2. INVESTIGATION SITES

The investigation site is located in the central part of Seto Inland Sea of Japan, which is surrounded by Honshu, Shikoku and Kyushu Islands, as shown in Figure 1. Seto Inland Sea is the biggest closed sea in Japan, and Kasaoka bay, located on the northern part of the investigation site, is a small narrow bay. The investigation site is divided into four parts, i.e., A, B, C and D. There are heavy industry districts in Mizushima and Fukuyama.

The sediment samples were obtained on September 22 and November 17 in 2000, and March 21 to 22, April 26 to 28 and August 4 and 5 in 2001. Core samples were obtained using a box core sampler made of stainless steel with a sectional area of 10 X 10 cm². The core length was 1.5 m at maximum. After the sampler was raised up, one side of the walls of the core box was opened, as shown in Figure 2. The core samples of top 30 cm were cut every 3 cm in thickness and they were kept in 50 mL glass containers. A stainless steel knife was used to cut the core samples. The lower part of core samples was cut with every 20 cm, and kept in 2L glass containers. The glass containers were previously washed with acetone. Surface sediments were obtained using an Ekman grab sampler. The surface samples were also kept in glass containers. These samples were subjected to measurements of soil properties and contents of heavy metals.



Figure 2. A core sample obtained from the sea bottom.

3. MEASUREMENTS

In order to obtain the fundamental properties, physical and chemical properties were measured on the sediments. With contamination, concentration of 12 elements, Al, Ba, Cd, Co, Cu, Fe, Mn, Ni, P, Pb, Ti, and Zn, were measured using ICP (Inductively Coupled Plasma Spectrometer) analysis. PCB is measured with a gas chromatography (GC)

combined with a mass spectrometer (MS) and organotin compounds are measured with a gas chromatography.

4. RESULTS AND DISCUSSION

4.1 Physical and chemical properties of sediments

Examples of the physical and some chemical properties of the sediment samples are presented in Table 1. The water content of these silty-clay sediments is quite high. The water content ranges from 149 to 238%. The ignition loss of these sediments is less than 13%. The specific gravity of the sediment particles ranges from 2.50 to 2.70.

Table 1. Physical and chemical properties of Site C sediments.

site	Depth (cm)	Water content (%)	Specific gravity	Ignition loss (%)	Carbonate content (%)
C-1	7.5	-	2.65	1.4	0.36
C-2	1.5	161	2.50	9.5	0.46
C-3	1.5	202	2.68	11	0.12
C-4	1.5	206	2.70	11	0.74
C-5	1.5	149	2.66	9.7	2.68
C-6	1.5	238	2.70	12	0.31
C-7	1.5	231	2.52	13	0.41

4.2 Lead

The vertical distributions of Pb contents are shown in Figure 3. From the data shown in Fig.3, the background value of Pb seems to be approximately 18-20 mg/kg. Figure 3 also shows that Site A is considerably contaminated with Pb, in comparison to Sites B and C. It seems that the contaminated thickness of sediments with Pb is 50 cm at minimum. The maximum thickness of contaminated layer may exceed 200 cm.

As described, the excess concentrations will cause serious bio-concentration and threaten human health. With this point, the background value will be a criterion for safety. The background value of substances in sediments can be defined as concentration of the substance of natural sediments without human influence. This value can be obtained from sediments deposited before approximately 1750, i.e., before Industrial Revolution. In fact, Murozumi et al (1969) found that lead concentration in Greenland glacier started increasing since 1750.

The background value of elements is defined as the concentration which is not affected by human activities. However, the background values of elements in marine sediments are not constant, but vary with type of sediments and the distance from coastal line or river mouth (Fukue et al, 1995). Generally, the fine particles have higher background value than the coarse particles. This is due to

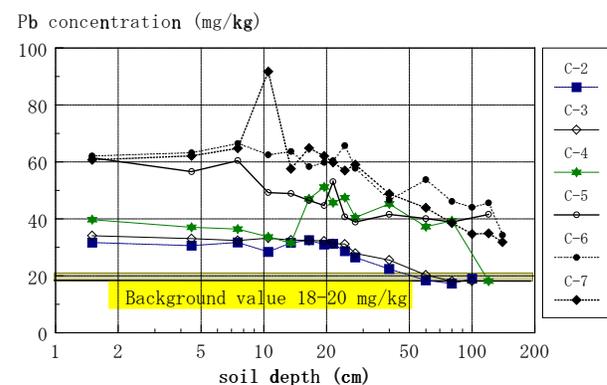
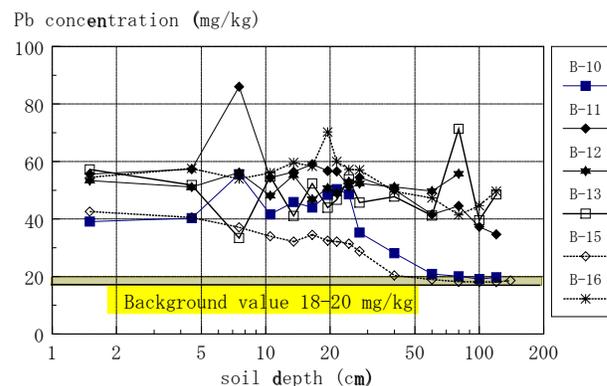
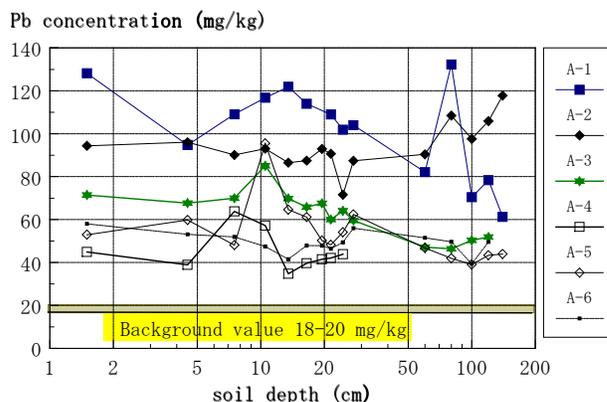


Figure 3. Vertical profiles of lead concentrations of Sites A, B and C.

the surface activities of particles, such as the density of electrical charge and specific surface area.

4.3 Background value

The background value of substances depends on at least the type of sediments. This may lead to a difficulty for evaluating the contamination of sediments. However, the approximate background values are obtained on various types of sediments. For examples, typical marine sediments are silty clays and their background values were obtained by the previous studies (Matsumoto, 1983, Matsumoto et al, 1983, Fukue et al, 1995, Fukue et al, 1999), as shown in

Table 2. Some of the elements shown in Table 2 have a wide range of background values, because of the varied nature of sediments.

Table 2. Background values of elements for marine silty soils (after Matsumoto, 1983, Matsumoto et al, 1983, Fukue et al, 1995, 1999)

Element	Hg	Cd	As	Pb
	mg/kg	mg/kg	mg/kg	mg/kg
Background value	0.05	0.1	10	18-20
Element	V	Zn	Cr	P
	mg/kg	mg/kg	mg/kg	mg/kg
Background value	45-100	50-150	60	230-650
Element	Cu	Ti	TBT	TPT
	mg/kg	g/kg	(µg/kg)	(µg/kg)
Background value	7-53	1.9-4.2	□	□

4.4 Copper

Figure 4 shows the horizontal distribution of Cu concentration for the surface sediments in the investigation sites. The concentrations of Cu are denoted with the bars, as shown in Figure 4. The highest concentration is 104 mg/kg at Site C7, and the lowest value is 4.8 mg/kg at Site D1 (see Figure 1).

4.5 Zinc

The vertical profiles of zinc concentrations at B and C Sites are shown in Figures 5 and 6. As the background value of zinc for silty sediments is about 100 mg/kg, as indicated in Table 2, it is obvious that the sediments are considerably contaminated with Zn. This is discussed later. The contaminated thickness with Zn is approximately 100 cm.

4.6 PCB and pesticide

The concentrations of PCB and a pesticide were measured on some sediment samples, but they were not detected. Though a large amount of pesticide was sprinkled on the pine trees near Kasaoka Bay about twenty years ago, the pesticide has been degraded.

4.7 Degree of pollution

If the background values are obtained, the contamination is evaluated with the degree of pollution. Fukue et al (1999) defined the degree of pollution as follows:

$$Pd = \frac{Ci - Bi}{Bi} \quad [1]$$

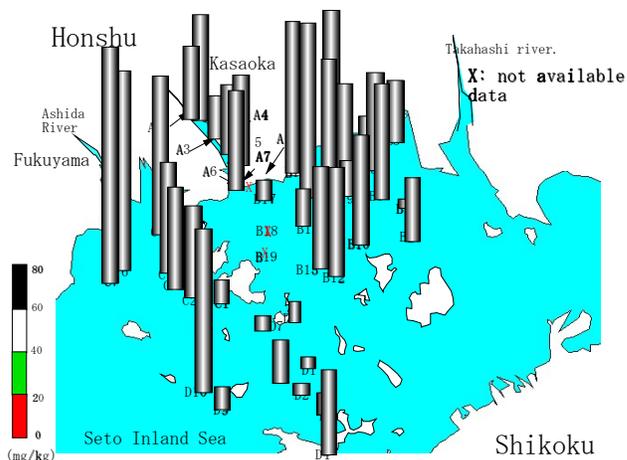


Figure 4. Cu concentrations of surface sediments in the investigation sites.

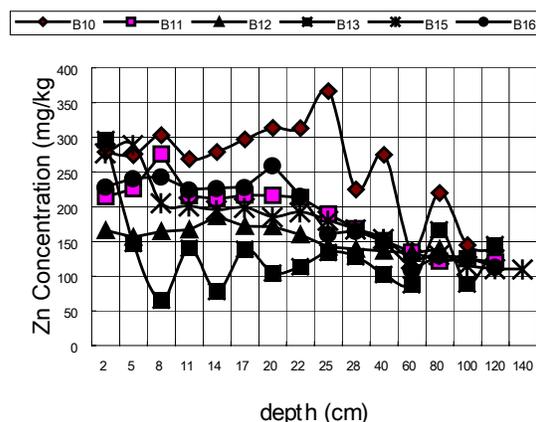


Figure 5. Vertical profiles of Zn concentration for the sediments in Site B.

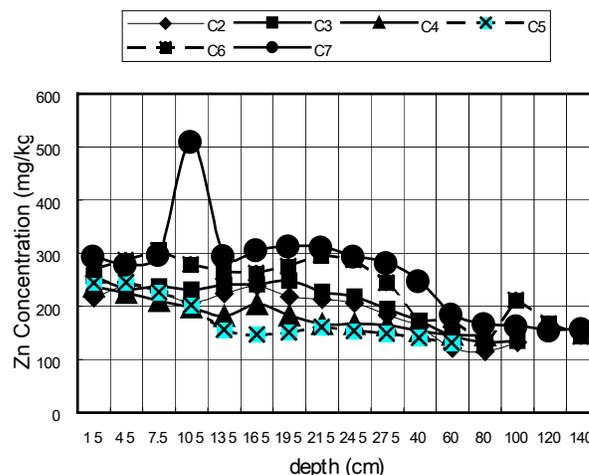


Figure 6. Vertical profiles of Zn concentration for the sediments in Site C

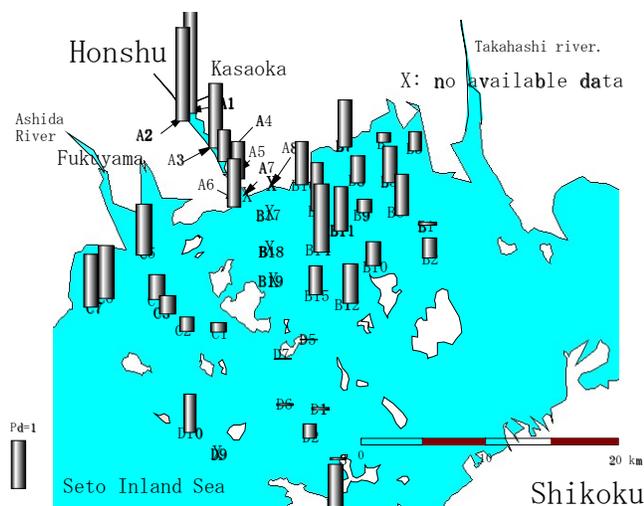


Figure 7. Pd values of lead for surface sediments in the investigation sites.

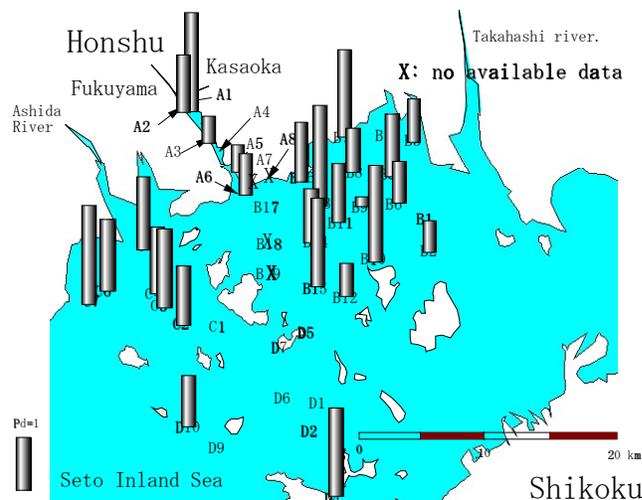


Figure 8. Pd values of zinc for surface sediments in the investigation sites.

where Pd is the degree of pollution, C_i is the present concentration at the depth considered and B_i is the background value with respect to the substance i . Apparently, Pd is zero when the sediments are not contaminated. It is natural that the higher the Pd value, the more contaminated the sediments are.

Figure 7 shows Pd values of Pb for the surface sediments in the investigation sites. The background value of Pb was assumed to be 20 mg/kg. The highest Pd value calculated by [1] is 5.4 at Site A1 and relatively high in Kasaoka Bay (at A sites), while Pd values are zero at Sites D1, D7 and D9 and very low at D5, D6, D7. This implies that the lead was discharged from the land and transported into the sea.

Figure 8 shows Pd value of Zn for the surface sediments in the investigation sites, where the background value is assumed to be 100 mg/kg. The Pd value is zero or negative at B1, B17, C1, D1 to D3, D5 to D7 and D9. The negative values are attributed to the actual lower background of the coarser sediments. The trend shown in Figure 8 is similar to the case of lead shown in Figure 7.

At present, there is no criterion on "danger or safety" with respect to the Pd value. Considering that sea animals are contaminated with hazardous substances, the criterion should be established and the measure should be taken.

4.8 Particle size and concentration

Since some ions of heavy metals are adsorbed to the sediment particles, the maximum concentrations primarily depend on particle sizes. Figure 9 shows that Cu concentration for sediments tends to increase with the increase of the fine fraction contents. This is because there is a capacity of the adsorption in relation to particle characteristics, i.e. surface area and charge density. The amount of adsorption is also determined by the equilibrium

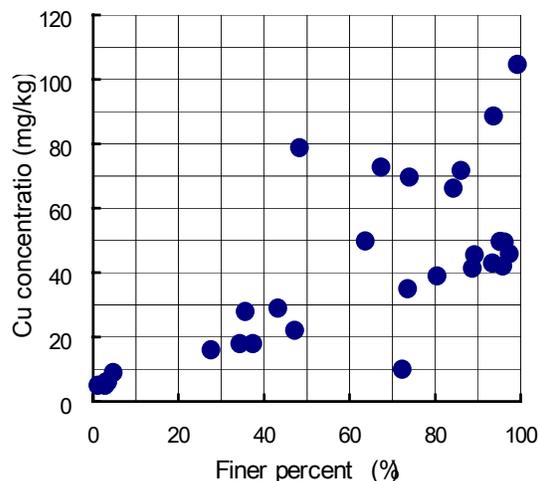


Figure 9. Cu concentration versus fine fraction content for sediments.

concentration under the maximum adsorption capacity. Therefore, the concentration of heavy metals for sediments may depend on the particle characteristics and equilibrium concentration at the time of adsorption. The adsorbed heavy metals can't be easily released, as discussed later.

5. LEACHING CHARACTERISTICS OF SEDIMENTS

The food chain is often assumed to occur from seawater. In many cases, the sediments examined are considered to be non-contaminated, because the adsorbed hazardous substances are hardly released in the leaching test. However, many kinds of benthos will assimilate fine particles (sediments) to absorb the organic matter adhered

on them. Therefore, it is noted that there is a food chain starting from the sea bottom.

On the other hand, the leaching characteristics of sediments are important to know the fate and transport of hazardous substances after the deposition of particles.

In leaching tests, about 10 g samples with a water content of 180 percents were washed with 275 ml distilled water and a solution with a pH of 4, for 6 hours, respectively. The concentrations of heavy metals for the leaching tests were calculated using the dry weight of the sediments and the concentration of solutes in the leachates.

The results are shown in Table 3, which shows that Pb, Cu and Zn are little released from the sediments by washing with distilled water. In the case of zinc, the decrease in pH value caused the increase in the concentration. This trend is well known as pH-dependency of adsorption capacity (Yong, et al, 1992).

Table 3. Results of the leaching tests.

	sediments (mg/kg)	Leaching test	
		(mg/kg)	(mg/kg)
washing		distilled water	pH4
Pb	66.6	less than 0.028	less than 0.028
Cu	75.6	less than 0.028	less than 0.028
Zn	354	0.691	14.1

In Japan, the environmental criteria of soil and water qualities are mostly based on the results of leaching test. However, the particles have been subjected to leaching by the seawater during sedimentation. Therefore, little heavy metals from the deposited sediments will come out by the washing in leaching tests. This result, however, does not mean "the sediments are safe". As mentioned earlier, a food chain under marine condition will start from the sediments.

6 CONCLUSIONS

As a case study of contaminated sites, Seto Inland Sea in Japan was investigated. The results show that the sediments are contaminated by the human discharge. The surface sediments from about 50 to more than 200 cm are contaminated with Cu, Zn and Pb, etc.

The degree of pollution defined is used to evaluate the contamination of sediments. The criteria in relation to *Pd* value are required to know the safety of sediments.

The contaminated concentration depends on the particle characteristics, specific surface area and charge density, etc, and also the equilibrium concentration at the time of deposition. Adsorbed heavy metals on sediment particles can't be easily released. Therefore, the leaching under usual conditions can't provide the desorption of heavy

metals. However, the change in pH value may promote the desorption of heavy metals.

The leaching test should not be used for the evaluation of sediment contamination, because of the food chain starting from the sea bottom.

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